

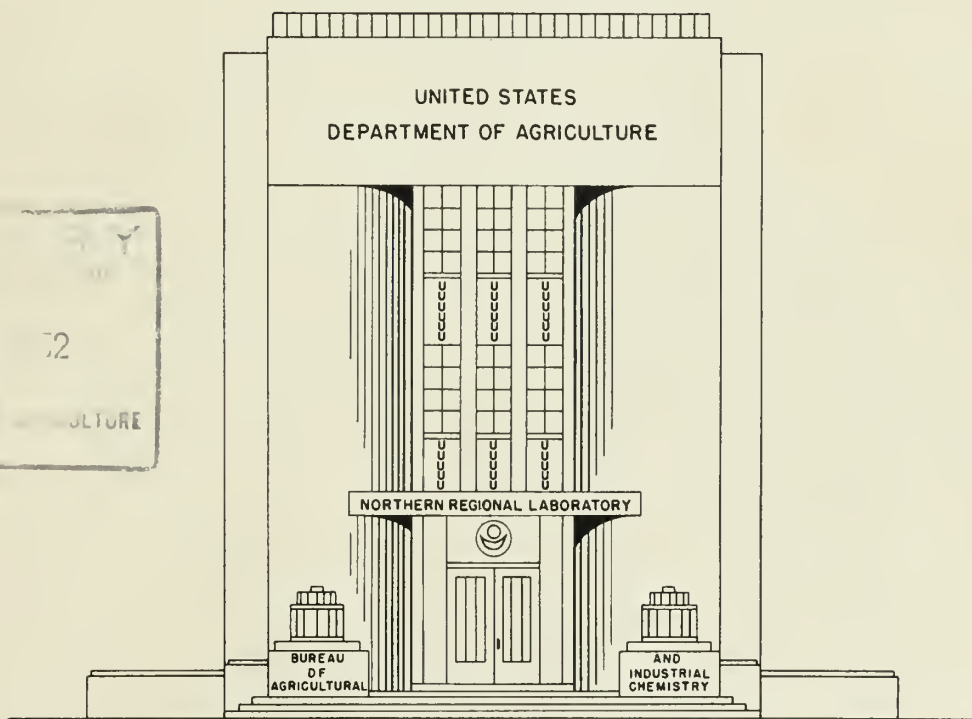
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UNITED STATES DEPARTMENT OF AGRICULTURE
Agricultural Research Administration
Bureau of Agricultural and Industrial Chemistry

X MONOGLYCERIDES FROM SOYBEAN OIL BY
HYDROLYSIS AND ESTERIFICATION X



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February 1952

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INTRODUCTION

Monoglycerides intended for use in shortenings and other food products are generally prepared by reacting fatty acids, fats, or oil with glycerine of high purity. Many patents have been issued (1,2,3,4,6)⁵ for novel methods of carrying out the reaction to obtain suitable emulsifiers for improving the properties of a number of food products. The use of monoglycerides has grown to such an extent that their acceptability is now widespread. During World War II the use of glycerine was restricted by Government regulation. In a severe emergency glycerine, as such, might not be available except for the most urgent military requirements, in which case none would be available for use in the preparation of monoglycerides. Experiments reported here were conducted for ascertaining whether monoglycerides, acceptable for use as emulsifiers in food products, could be prepared directly from soybean oil without using glycerine purchased on the open market. The method finally developed is based on the preparation of monoglycerides from soybean oil by hydrolyzing the oil, removing two-thirds of the fatty acid layer formed by the hydrolysis, and reacting the glycerine layer with the remainder of the fatty acids. This method, which obviates the use of purified glycerine, when carried out on a laboratory scale yielded a product entirely suitable for replacing a commercial monoglyceride product in an experimental cake recipe. Detailed cost estimates, based on these laboratory experiments, are not justified at this time. However, rough calculations indicate that, after allowing credit for the by-product fatty acids, the net cost of raw materials for producing monoglycerides by this method is slightly less than that for producing them from soybean oil and glycerine. Possible modifications of the method described here may become apparent to those engaged in the production of monoglycerides, and it is probable that certain changes in the procedure may be desirable from an economic or technical standpoint. It is considered probable that both the splitting of the oil and esterification could be carried out in a single reaction vessel of suitable design.

¹ Report of a study made under the Research and Marketing Act of 1946. Presented at meeting of the American Oil Chemist Society, New Orleans, Louisiana, May 1-3, 1951.

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⁵ Italic numbers of parentheses refer to Literature Cited, page 4.

It might be expected, from a review of the patent literature, that soybean oil would undergo considerable deterioration during the hydrolysis and esterification reactions, since it contains appreciable unsaturation. That this is not the case is shown by the fact that very little darkening of the product occurs. What darkening does occur is not detrimental to the final product and probably could be reduced by slight improvements in methods of handling the products between the hydrolysis and esterification steps.

METHOD

The following method was used to prepare a sufficient quantity of monoglycerides for evaluation in cake baking experiments.

Soybean oil, which had been refined, bleached, and deodorized, was placed in a 2-liter autoclave with an equal weight of distilled water. To remove as much air as possible, the system was evacuated to a pressure of 3 millimeters until the temperature of the reactants reached 40° C. The oil was then hydrolyzed at 500 pounds per square inch gauge (p.s.i.g.) and 240° C. for 2 1/2 hours. The autoclave was constructed of type 316 stainless steel and was equipped with electrical heaters, an agitator consisting of 2-inch blades which revolved at about 700 r.p.m., and connections for a pressure gauge and for a tube for the removal of samples. After 2 1/2 hours at 240° C., the oil was 91 percent hydrolyzed. The acid layer contained 5 percent of monoglycerides.

After the autoclave had been cooled to 50° C., the contents were placed in a separatory funnel. The aqueous glycerol phase was separated and placed in a three-necked round bottom Pyrex flask fitted with a sealed-in stirrer, thermocouple well, and a steam-heated reflux condenser which was connected to a water-cooled condenser and a condensate receiver. Provision was also made for removing samples from the flask during the reaction. The receiver was connected to a vacuum pump through a manostat which controlled the vacuum on the system.

The flask was placed under a vacuum (30 to 50 mm. absolute pressure) and heated at 70° to 90° C. until all the water substantially was evaporated from the glycerol. The glycerol was then cooled to 50° C. and a third of the fatty acid layer and an aqueous solution containing 0.1 percent of sodium hydroxide, based on the weight of acids, were added. The flask was then placed under an absolute pressure of 103 to 105 millimeters and heated to 220° C. Considerable water was removed at about 90° C. together with small amounts of materials which apparently were fatty acids. The condensate created an emulsion which occasionally formed a temporary plug in the condenser. The temperature was held at 220° C. for 1 1/2 hours and samples were removed at 30-minute intervals for analysis. The flask was then cooled in about 10 minutes to 50° C., and the stoichiometric amount of dilute phosphoric acid was added to neutralize the sodium hydroxide catalyst. The contents of the flask was stirred vigorously, 1 percent of an acid-activated clay was added, and then the reaction mixture momentarily was heated to 100° C. under vacuum. The mixture was then cooled to 50° C., and the monoglyceride product was filtered through a Buchner funnel.

DISCUSSION

Preliminary studies of the hydrolysis and esterification reactions were carried out because insufficient published data were available at the time for accurately predicting the course of these reactions. Recently Sturzenegger and Sturm (7) have

reported extensive data on the neutral hydrolysis of certain vegetable oils. Although the data given here represent only single experiments for each condition, they appear to be fairly consistent.

Figure 1 shows the extent of hydrolysis of refined, bleached, deodorized soybean oil, at 500 p.s.i.g. pressure and 240° C., when three different ratios of water to oil were used. The reactions were carried out, with no catalyst present, in the 2-liter autoclave. Samples were removed at intervals and analyzed for the extent of hydrolysis, which was calculated as the ratio of alcoholic potassium hydroxide required for neutralization of the fatty acids to the total amount required for neutralization and saponification of the acid layer. The reaction could be accelerated by the addition of 0.1 percent of sodium hydroxide, but a batch which was hydrolyzed with this catalyst was darker than the products prepared without catalyst. The removal of air from the autoclave before the oil was heated above 50° C. probably was important for obtaining a light-colored product. The maximum degree of hydrolysis was attained in about 2 1/2 hours at 240° C.

The esterification reaction was carried out both with and without catalyst at three temperatures; 180° C., 200° C., and 220° C. Figure 2 shows the decrease in free fatty acid content, figure 3 shows the increase in monoglyceride content, and figure 4 shows the disappearance of glycerine as the reactions proceeded, under each of these conditions. Monoglyceride and glycerine analyses were made by the method of Pohle and Mehlenbacher (5).

Temperatures above 200° C. apparently do not favor the formation of monoglycerides when no catalyst is used, although when 0.1 percent of sodium hydroxide was used as a catalyst the three temperatures were equally effective for monoglyceride production. It is conceivable that the apparently erratic results which were obtained when a catalyst was not used were due to insufficient agitation and, therefore, insufficient dispersion of glycerine with the monoglyceride layer. On the other hand, the sodium hydroxide catalyst probably promotes emulsification of the two layers.

The monoglycerides prepared in the manner described were submitted for evaluation to a commercial organization possessing technical knowledge and practical experience in the field of cake baking. At the research laboratory of that firm, the monoglycerides were incorporated in hydrogenated vegetable fat at various percentages in order to make glycerinated shortenings. The shortenings were evaluated by comparing them, as ingredients in white cakes, with a commercial vegetable shortening containing monoglycerides, that is, the type of shortening commonly used for baking cakes. It was found that, as the percentage of monoglyceride was raised, the cake volume increased, and the overall physical characteristics of the cake were enhanced. The cakes containing soybean monoglycerides in concentrations of 1.0 and 1.25 percent were comparable in all respects with those made from the commercial shortening. The tests indicated that this particular type of soybean monoglycerides should be entirely suitable as the emulsifying agent in the commercial production of cake shortenings.

The authors appreciate the valuable suggestions and criticisms of R. T. Milner, C. T. Langford, and O. L. Brekke of the Northern Regional Research Laboratory during the course of this investigation.

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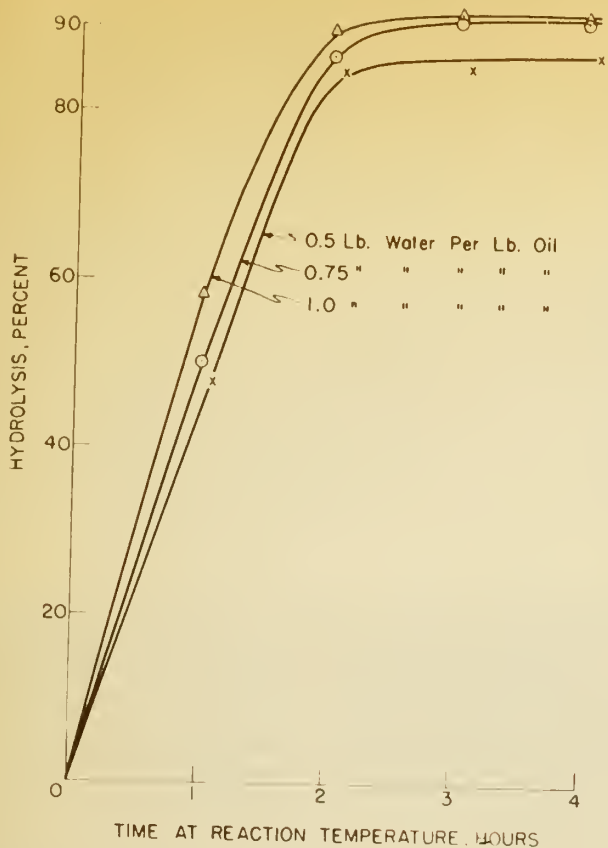


Figure 1.-- Hydrolysis of refined, bleached, and deodorized soybean oil at 500 p.s.i.g. and 240° C.

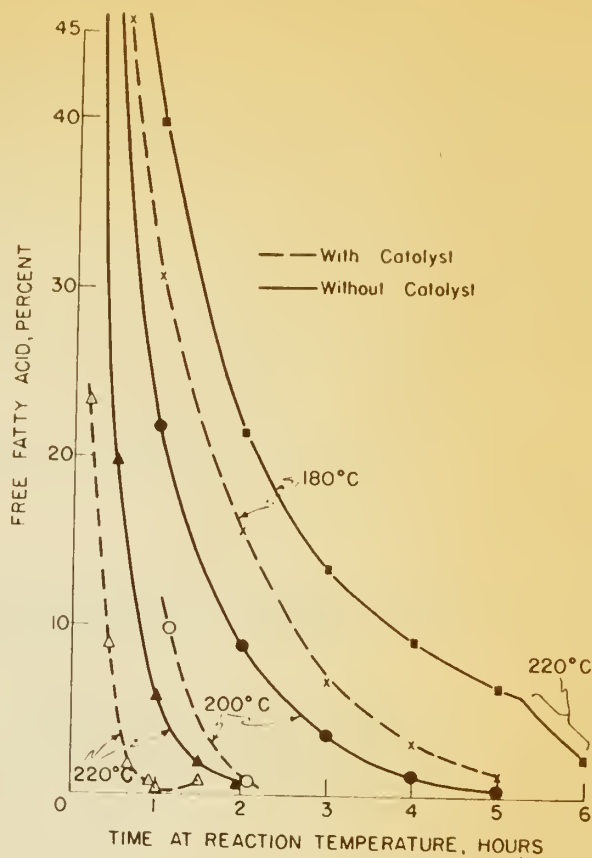


Figure 2.-- Disappearance of fatty acids during preparation of monoglycerides.

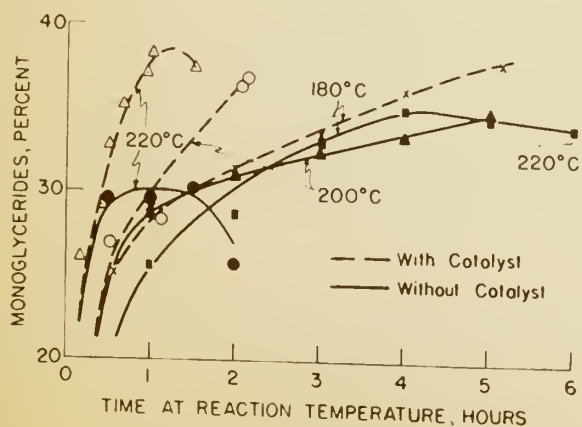


Figure 3.-- Monoglyceride production by the esterification of fatty acids and glycerine obtained from hydrolysis of soybean oil.

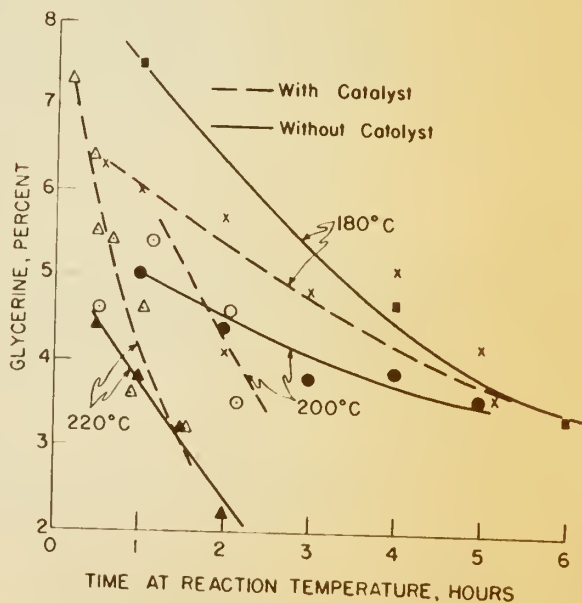


Figure 4.-- Disappearance of glycerine during preparation of monoglycerides.

